

FORM PTO-1390 (Modified) (REV 11-98)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>JMYT-237US</b>	
<b>TRANSMITTAL LETTER TO THE UNITED STATES</b> <b>DESIGNATED/ELECTED OFFICE (DO/EO/US)</b> <b>CONCERNING A FILING UNDER 35 U.S.C. 371</b>				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) <b>To Be Assigned 09/807343</b>	
INTERNATIONAL APPLICATION NO. <b>PCT/GB99/03281</b>		INTERNATIONAL FILING DATE <b>04 October 1999 (04.10.99)</b>		PRIORITY DATE CLAIMED <b>12 October 1998 (12.10.98)</b>	
TITLE OF INVENTION <b>PROCESS AND APPARATUS FOR TREATING COMBUSTION EXHAUST GAS</b>					
APPLICANT(S) FOR DO/EO/US <b>TWIGG, Martyn Vincent</b>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</li> <li>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2))           <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> has been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li>7. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> <li>8. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))           <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> have been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input checked="" type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>9. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>10. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li>11. <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li>12. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> </ol>					
<b>Items 13 to 20 below concern document(s) or information included:</b>					
<ol style="list-style-type: none"> <li>13. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>15. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li>16. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>17. <input type="checkbox"/> A substitute specification.</li> <li>18. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>19. <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail</li> <li>20. <input type="checkbox"/> Other items or information:</li> </ol>					

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) <b>09/807343</b>		INTERNATIONAL APPLICATION NO. <b>PCT/GB99/03281</b>		ATTORNEY'S DOCKET NUMBER <b>JMYT-237US</b>	
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21. The following fees are submitted:				<b>CALCULATIONS PTO USE ONLY</b>	
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b> <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... <b>\$970.00</b> <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$840.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$690.00</b> <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$670.00</b> <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$96.00</b> <p style="text-align: center;"><b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b></p>				<b>\$860.00</b>	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				<b>\$0.00</b>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	23 - 20 =	3	x \$18.00	<b>\$54.00</b>	
Independent claims	2 - 3 =	0	x \$80.00	<b>\$0.00</b>	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$914.00</b>	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>SUBTOTAL =</b>				<b>\$914.00</b>	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				<b>\$0.00</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$914.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$914.00</b>	
				Amount to be: refunded	\$
				charged	\$

☒ A check in the amount of **\$914.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **18-0350** A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

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SIGNATURE

**Christopher R. Lewis**  
\_\_\_\_\_  
NAME

**36,201**  
\_\_\_\_\_  
REGISTRATION NUMBER

**April 12, 2001**  
\_\_\_\_\_  
DATE

JMYT-237US

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Martyn Vincent Twigg : Art Unit:  
Application No.: To Be Assigned : Examiner:  
Filed: Herewith :  
FOR: PROCESS AND APPARATUS FOR :  
TREATING COMBUSTION EXHAUST GAS :

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Washington, DC 20231

SIR:

Prior to examination, please amend the above-identified application as follows.

IN THE CLAIMS:

Please replace claims 1, 4-7, 9-12, 14-16, and 18-21 with the following amended claims.

1 1. (Amended) A system for treating combustion exhaust gas,  
2 which system comprising: a catalyst effective to promote oxidation of at least NO  
3 to NO<sub>2</sub>; a filter downstream of the oxidation catalyst, which filter being effective to  
4 collect soot and hold it for combustion reaction with the NO<sub>2</sub> in the gas; a NO<sub>x</sub>  
5 absorber downstream of the filter, which NO<sub>x</sub> absorber is charged with solid  
6 adsorbent; means for introducing intermittently a regenerant of the absorber, which  
7 means being effective to inject a NO<sub>x</sub>-specific reactant upstream of the absorber;  
8 and a catalyst system effective to promote reactions of hydrocarbons (HC) and CO  
9 with O<sub>2</sub> to H<sub>2</sub>O and CO<sub>2</sub> and to treat NO<sub>x</sub> to N<sub>2</sub>, wherein said catalyst system is at  
10 least one of: (1) associated with the absorber; or (2) located downstream of the  
11 absorber.

1 4. (Amended) A system according to claim 1, wherein the NO<sub>x</sub>  
2 absorbent comprises at least one of: (a) compounds of alkali metals, alkaline earth  
3 metals, rare earth metals and transition metals or a mixed oxide of any two or more  
4 thereof; and (b) zeolites, carbons and/or high surface area oxides.

- 1 5. (Amended) A system according to claim 4, wherein the  
2 mixed oxide is selected from the group consisting of Ba-Cu-O and MnO<sub>2</sub>-BaCuO<sub>2</sub>.
- 1 6. (Amended) A system according to claim 1, wherein the  
2 catalyst system comprises at least one of vanadia/titania and one or more platinum  
3 group metal.
- 1 7. (Amended) A system according to claim 1, wherein the  
2 injection means is arranged to inject the reactant upstream of the filter.
- 1 9. (Amended) A system according to claim 1, wherein the  
2 injection means is arranged to inject the reactant downstream of the filter.
- 1 10. (Amended) A system according to claim 1, wherein the filter  
2 is catalysed.
- 1 11. (Amended) A system according to claim 1, wherein the  
2 injection means is for injecting ammonia, hydrazine, urea or aqueous urea solution.
- 1 12. (Amended) A system according to claim 1, further including  
2 sensors, indicators, computers and actuators, effective to maintain operation within  
3 desired conditions.
- 1 14. (Amended) A diesel engine including a system according to  
2 claim 1.
- 1 15. (Amended) An engine according to claim 14, which is a  
2 turbo-charged direct injection engine.
- 1 16. (Amended) A process for treating combustion exhaust gas  
2 containing CO, hydrocarbons (HC), NO, O<sub>2</sub>, soot and non-reactive gases,  
3 comprising the steps of: (i) catalysing oxidation of NO to NO<sub>2</sub>; (ii) collecting soot  
4 on a filter; (iii) combusting the collected soot by reaction with NO<sub>2</sub>; (iv) removing  
5 NO<sub>x</sub> from the product of step (iii) by contacting a regenerable NO<sub>x</sub> absorbent with  
6 gas containing NO<sub>x</sub>; (v) regenerating the absorbent intermittently by injecting a  
7 NO<sub>x</sub>-specific reactant upstream of the absorbent; and (vi) at least during step (v),  
8 contacting a catalyst system effective to promote reactions of HC and CO with O<sub>2</sub>  
9 to H<sub>2</sub>O and CO<sub>2</sub> and to react NO<sub>x</sub> to N<sub>2</sub> with the gas product of step (v).
- 1 18. (Amended) A process according to claim 16, wherein the  
2 NO<sub>x</sub>-specific reactant is ammonia or hydrazine and is injected as such or as a  
3 precursor compound decomposable thereto *in situ*.

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1 19. (Amended) A process according to claim 18, wherein the  
2 precursor is urea or aqueous urea solution.

1 20. (Amended) A process according to claim 16, wherein the  
2 exhaust gas is the product of combustion of fuel containing less than 50 ppm w/w  
3 of sulphur.

1 21. (Amended) A process according to claim 16, operated in  
2 compliance with the European Stage IV emission legislation.

Please add the following new claims:

1 22. (Newly Added) A process according to claim 16,  
2 wherein step (iii) comprises combusting the collected soot by reaction with  
3 NO<sub>2</sub> and further with O<sub>2</sub> left over after step (i).

1 23. (Newly Added) A system according to claim 5, wherein  
2 the mixed oxide further comprises at least one of CeO<sub>2</sub>, Y-Ba-Cu-O and Y-Sr-  
3 Co-O.

Respectfully submitted,



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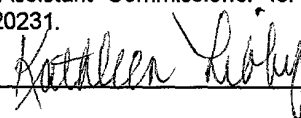
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I hereby certify that this paper and fee are being deposited, under 37 C.F.R. § 1.10 and with sufficient postage, using the "Express Mail Post Office to Addressee" service of the United States Postal Service on the date indicated above and that the deposit is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

The Assistant Commissioner for Patents is hereby authorized to charge payment to Deposit Account No. 18-0350 of any fees associated with this communication.

Kathleen Libby



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VERSION WITH MARKINGS TO SHOW CHANGES MADEIN THE CLAIMS:

1                   1.       (Amended) A system for treating combustion exhaust gas,  
2       which system comprising: a catalyst effective to promote oxidation of at least NO  
3       to NO<sub>2</sub>; a filter downstream of the oxidation catalyst, which filter being effective to  
4       collect soot and hold it for combustion reaction with the NO<sub>2</sub> in the gas; a NO<sub>x</sub>  
5       absorber downstream of the filter, which NO<sub>x</sub> absorber is charged with solid  
6       adsorbent; means for introducing intermittently a regenerant of the absorber, which  
7       means being effective to inject a NO<sub>x</sub>-specific reactant upstream of the absorber;  
8       and[, associated with and/or downstream of the absorber,] a catalyst system  
9       effective to promote reactions of hydrocarbons (HC) and CO with O<sub>2</sub> to H<sub>2</sub>O and  
10      CO<sub>2</sub> and to treat NO<sub>x</sub> to N<sub>2</sub>, wherein said catalyst system is at least one of: (1)  
11      associated with the absorber; or (2) located downstream of the absorber.

1                   4.       (Amended) A system according to claim 1, [2 or 3,] wherein  
2       the NO<sub>x</sub> absorbent comprises at least one of: (a) compounds of alkali metals,  
3       alkaline earth [metal] metals, rare earth metals and transition metals or a mixed  
4       oxide of any two or more thereof; [and/or] and (b) zeolites, carbons and/or high  
5       surface area oxides.

1                   5.       (Amended) A system according to claim 4, wherein the  
2       mixed oxide [includes] is selected from the group consisting of Ba-Cu-O[,] and  
3       MnO<sub>2</sub>-BaCuO<sub>2</sub>[, optionally including CeO<sub>2</sub>, Y-Ba-Cu-O or Y-Sr-Co-O].

1                   6.       (Amended) A system according to [any of claims] claim 1 [to  
2       5], wherein the catalyst system comprises at least one of vanadia/titania [and/or]  
3       and one or more platinum group metal.

1                   7.       (Amended) A system according to [any of claims] claim 1 [to  
2       6], wherein the injection means is arranged to inject the reactant upstream of the  
3       filter.

1                   9.       (Amended) A system according to [any of claims] claim 1 [to  
2       6], wherein the injection means is arranged to inject the reactant downstream of the  
3       filter.

1            10. (Amended) A system according to [any preceding] claim 1,  
2    wherein the filter is catalysed.

1 11. (Amended) A system according to [any preceding] claim 1,  
2 wherein the injection means is for injecting ammonia, hydrazine, urea or aqueous  
3 urea solution.

1                    12.    (Amended) A system according to [any preceding] claim 1,  
2    further including sensors, indicators, computers and actuators, effective to maintain  
3    operation within desired conditions.

1                    14.    (Amended) A diesel engine including a system according to  
2    [any preceding] claim 1.

1            15.    (Amended) An engine according to claim [8] 14, which is a  
2 turbo-charged direct injection engine.

1 16. (Amended) A process for treating combustion exhaust gas  
2 containing CO, hydrocarbons (HC), NO, O<sub>2</sub>, soot and non-reactive gases, [which  
3 process comprises] comprising the steps of: (i) catalysing oxidation of NO to NO<sub>2</sub>;  
4 (ii) collecting soot on a filter; (iii) combusting the collected soot by reaction with  
5 NO<sub>2</sub> [and possibly also O<sub>2</sub> left over after step (i)]; (iv) removing NO<sub>x</sub> from the  
6 product of step (iii) by contacting a regenerable NO<sub>x</sub> absorbent with gas containing  
7 [it] NO<sub>x</sub>; (v) regenerating the absorbent intermittently by injecting a NO<sub>x</sub>-specific  
8 reactant upstream of the absorbent; and (vi) at least during step (v), contacting a  
9 catalyst system effective to promote reactions of HC and CO with O<sub>2</sub> to H<sub>2</sub>O and  
10 CO<sub>2</sub> and to react NO<sub>x</sub> to N<sub>2</sub> with the gas [the] product of step (v).

1                   18.     (Amended) A process according to claim 16 [or 17], wherein  
2     the NOx-specific reactant is ammonia or hydrazine and is injected as such [and/or]  
3     or as a precursor compound decomposable thereto *in situ*.

1                    19. (Amended) A process according to claim [16, 17 or] 18,  
2 wherein the precursor is urea or aqueous urea solution.

20. (Amended) A process according to claim 16[ 17, 18 or 19],  
wherein the exhaust gas is the product of combustion of fuel containing less than 50  
ppm w/w of sulphur.

**Claims 22 and 23 have been added.**



## PROCESS AND APPARATUS FOR TREATING COMBUSTION EXHAUST GAS

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This invention concerns emission control especially for diesel engine exhaust gas.

EP-A-0341832 and corresponding US 4902487 describe a process and treatment system for removing soot from diesel exhaust gas containing NO by passing such gas unfiltered over an oxidation catalyst to convert NO to NO<sub>2</sub>, collecting the soot on a filter and using the resulting gas containing NO<sub>2</sub> to combust the collected soot, the amount of NO converted to NO<sub>2</sub> being sufficient to enable such combustion to proceed at a temperature less than 400C.

EP-A-0758713 describes a process in which such a soot combustion step is followed by removing NO<sub>x</sub> from the combustion outlet gas by means of a solid absorbent and regenerating the absorbent by intermittent engine fuel inlet adjustment or injection of reductant into the exhaust gas upstream of the oxidation catalyst. This process has disadvantages, for example requiring engine modification.

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According to the invention there is provided a process for treating combustion exhaust gas containing CO, HC, NO, O<sub>2</sub>, soot and non-reactive gases, by the steps:

- i. catalysing oxidation of NO to NO<sub>2</sub>;
- ii. collecting on a filter soot from the product of i;
- 25 iii. combusting the collected soot by reaction with NO<sub>2</sub> and possibly also any O<sub>2</sub> left over after the reactions in i;
- iv. removing NO<sub>x</sub> from the product of iii by the action of a regenerable NO<sub>x</sub> absorbent;
- v. regenerating the absorbent intermittently by:
  - 30 (a) decreasing the net oxidant level by injecting reductant upstream of the absorber but downstream of the oxidation catalyst; and/or
  - (b) injecting a NO<sub>x</sub>-specific reactant upstream of the absorbent; and
- vi. at least during said regeneration, subjecting the gas leaving the absorbent to a catalyst system effective to promote reactions of HC and CO with O<sub>2</sub> to H<sub>2</sub>O and
- 35 CO<sub>2</sub> and of NO<sub>x</sub> to N<sub>2</sub>.

The invention provides a treatment system for such exhaust gas comprising catalysts and absorbent corresponding to the process steps, in particular, in combination and in order: a catalyst effective to promote oxidation of at least NO to NO<sub>2</sub>; a filter effective to collect the soot and hold it for combustion reaction with the NO<sub>2</sub> in the gas; a NO<sub>x</sub> absorber charged with solid absorbent; means for introducing intermittently a regenerant of the absorber, such means being effective to introduce reductant upstream of the absorber but downstream of the oxidation catalyst; and/or to introduce a NO<sub>x</sub>-specific reactant upstream of the absorber; and, associated with or downstream of the absorber a catalyst system effective to promote reactions of HC and CO with O<sub>2</sub> to H<sub>2</sub>O and CO<sub>2</sub> and of NO<sub>x</sub> to N<sub>2</sub>.

In addition, the system may include routine features, for example means to adjust the temperature of the gas to the level required in the next downstream chemical step.

The system may be structured within a single housing ("can"), or in separated housings according to engine design and under-floor or other space considerations. Thus for example for V-engine configurations, some or all of the elements of the system may be disposed in parallel.

The catalysts and absorbent are suitably supported on a ceramic or metal honeycomb, the ceramic comprising one or more of alumina, silica, titania, cordierite, ceria, zirconia, silicon carbide or other, generally oxidic, material. The honeycomb carries a washcoat and, in one or more layers thereon, the active catalytic and/or absorptive material, to be described in more detail below. The honeycomb has typically at least 50, for example 50-400, cells per square inch, possibly more, eg up to 800, or up to 1200 if composed structurally of metal. Generally the range 200-800 is preferred for the catalysts and absorbent.

In the oxidation catalyst the active material comprises generally a platinum group metal ("PGM"), especially platinum and/or palladium, optionally with other PGMs, eg rhodium, and other catalytic or promoting components. The exact compositions and structure of the oxidation catalyst are not critical to operation of the invention, and hence may be varied according to the requirements of the situation. A low temperature light-off formulation

is generally preferred. Conventional manufacturing techniques may be used. The catalyst should of course be sized and composed to achieve the necessary conversions, and the design should minimise trapping of soot within its honeycomb.

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The filter may be any capable of trapping the soot without causing excessive back-pressure. In general, ceramic, sintered metal or woven or non-woven wire filters are usable, and wall-flow honeycomb structures may be particularly suitable. The structural material of the filter is preferably porous ceramic oxide, silicon carbide or sintered metal. A coating such as alumina, and also a catalyst such as one or more PGMs (eg Pt with MgO) or La/Cs/V<sub>2</sub>O<sub>5</sub> may be present. The soot is generally carbon and/or heavy hydrocarbons, and is converted to carbon oxides and H<sub>2</sub>O. Certain embodiments of this principle are in commercial use in Johnson Matthey's Continuously Regenerating Trap technology, and are described in the above-mentioned EP-A-0341832 and US 4902487, the teaching of which is incorporated herein by reference.

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The NO<sub>x</sub> absorbent (referred to also as a "NO<sub>x</sub>-trap"), to be described further below, may be provided in one unit or a succession of separate units. It may be in the form of active layers on a conventional honeycomb substrate, or may be in the form of serial deposits on a single honeycomb or possibly multiple honeycombs.

20

The absorbent may be selected from:

- (a) compounds of alkali metals, alkaline earth metals, rare earth metals and transition metals, capable of forming nitrates and/or nitrites of adequate stability in absorbing conditions and of evolving nitrogen oxides and/or nitrogen in regenerating conditions; and/or
- (b) adsorptive materials such as zeolites, carbons and high-area oxides.

25

Compounds (a) may be present (before NO<sub>x</sub> absorption) as composite oxides, eg of alkaline earth metal and copper such as Ba-Cu-O or MnO<sub>2</sub>-BaCuO<sub>2</sub>, possibly with added Ce oxide, or Y-Ba-Cu-O and Y-Sr-Co-O. (The oxides are referred to for simplicity, but in practice hydroxides, carbonates and nitrates are present, depending on the temperature and gas composition). Whichever compounds are used, there may be present also one or more

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catalytic agents, such as precious metals, effective to promote such reactions as the interchanges of the nitrogen oxides and the action of reductant and/or NO<sub>x</sub>-specific reactant.

5           The catalyst system for step vi can be any that is active at the prevailing temperature and not adversely affected by exposure to lean gas between regeneration periods. It may be associated with the absorbent or may, alternatively or additionally, be in a separate bed. Typically it comprises one or more PGMs, especially Pt, Rh, Pd and combinations thereof, on a high-surface washcoat on a honeycomb structure as described above. Suitable catalysts are  
10 of the '3-way' or 'SCR' type. Many others have been described in the literature and are available to skilled persons.

          If that catalyst system is associated with the absorbent, that is, the absorber is 'catalysed', the catalytic material may be for example co-precipitated or co-impregnated or co-  
15 deposited with NO<sub>x</sub> absorbent or present as one or more sandwiched layers or as fine (eg 10-500 microns) particles on or in a layer of absorbent or among particles of absorbent.

          For regeneration of the NO<sub>x</sub> absorber:

1. as reductant, hydrocarbon may be introduced, for example gasoline or diesel fuel, which is  
20 especially convenient, or another such as light oil, kerosene or a C3 to C8 paraffin;
2. as reductant, there may be injected hydrogen (suitably generated in situ on board the vehicle) or a readily dehydrogenatable reductant such as a lower alcohol, especially methanol or ethanol. If reductant is injected as specified, that is, downstream of the oxidation catalyst, introduction of the same or a different reductant upstream of the  
25 oxidation catalyst, possibly by engine management, eg to provide for reaction increasing gas temperature, is not excluded, but is controlled to give gas lean enough for absorption of NO<sub>x</sub> to continue. The intermittent reductant injection downstream, of the oxidation catalyst then decreases the oxidant content to a NO<sub>x</sub> desorption level;
3. a preferred technique comprises injecting a NO<sub>x</sub>-specific reactant, especially a nitrogen  
30 hydride for example ammonia or hydrazine. This can be injected as such or as a solution in eg water or as a precursor compound, for example urea or aqueous urea solution, producing the reactant in exhaust treatment conditions. Such compounds are referred to herein as 'ammonia' at stages after injection. Injectors for such reactants or compounds,

possibly using carrier gas such as air, have been published.

For regeneration using a NO<sub>x</sub>-specific reactant, the oxidant level can be decreased less, if at all, than when using reductant. Indeed the reactant may be used especially in lean conditions, for example:

(a) exhaust gas as generated by the engine or as issuing from a preceding step of exhaust treatment;

(b) such gas to which reductant short of equivalence has been or is being added;

(c) gas made leaner, for example when the reactant is injected with the aid of air.

Regeneration using NO<sub>x</sub>-specific reactant is also effective in:

(d) rich or equivalent gas and also in gas into which reductant has been introduced eg to provide for reaction increasing gas temperature but leaving the gas net-lean in composition.

The point of injection of the reactant may most simply be downstream of the filter; in this event the temperature is typically in the range 150°-300°C. However, injection may be earlier: if upstream of the filter but downstream of the oxidation catalyst, the temperature is typically in the range 250°-350°C at filter inlet, as required for soot combustion. Further, the reactant may be injected upstream of the oxidation catalyst. Since in such earlier injection the fed reactant is at a 'spike' concentration to react with NO<sub>x</sub> to be evolved over the short period of regeneration of the absorber, it is in substantial excess over the NO<sub>x</sub> in the flowing exhaust gas and consequently need not suffer much loss by reaction with NO<sub>x</sub>. If in an extreme case it were to react with all the flowing NO<sub>x</sub> to give N<sub>2</sub> or N<sub>2</sub>O, this would stop combustion of soot on the filter: however, owing to the shortness of the ammonia injection spike, any accumulation of soot would be small and combustion would be resumed before blockage took place. The temperature should not be high enough to give substantial oxidation of ammonia to NO<sub>x</sub> over the oxidation catalyst. To limit unwanted side-reactions of ammonia, it may be introduced as a precursor compound, thus delaying availability of ammonia. Such limitation may also be provided by suitable formulation of the oxidation catalyst and/or filter. In particular, the filter may be of the non-catalysed type, free of deliberately introduced catalytic material such as PGM. Any fortuitous catalytic activity of the filter, due for example to its structural material or accumulated deposits such as carbon,

appears not to seriously promote such side-reactions.

5 The rate of provision of the reactant should be as nearly as possible stoichiometric to the quantity of NO<sub>x</sub> to be reacted. Especially when injection is to be upstream of the filter, the rate should be controlled in response to measurements of final exit NO<sub>x</sub> and ammonia. In the process using the reactant there may also be enrichment of the gas by introduction of non-specific reductant.

10 Decrease of net oxidant level by injection of reductant between the oxidation catalyst and the filter or (preferably) between the filter and the absorbent to provide least interference with soot combustion, suitably produces a gas composition corresponding to an air/fuel weight ratio in the range 10 to equivalence.

15 Usually the regeneration phase can be a small fraction, eg 0.1% to 5%. of engine running time, depending of course on operating conditions.

20 The invention provides also an engine in combination with the system and a process of operating such an engine. The combination may include established expedients such as electric heating, EGR, or recycle of released NO<sub>x</sub> to one or more points upstream of the soot filter.

Control of the process and engine, in particular the means to regenerate the NO<sub>x</sub> absorber, includes for example:

- 25 1. response to ultimate detection of NO<sub>x</sub> or ammonia leakage from the absorber and/or final exit gas;
2. response to prediction based on input of data on deliberate or load-responsive engine management variation;
- 30 3. allowance for gas composition variations, for example non-steady conditions such as incomplete warm-up or weather. In particular, injection is timed to occur when the temperature is at a level permitting regeneration.

Thus the combination may include sensors for at least one of: fuel composition; air/fuel ratio at engine inlet; exhaust gas compositions and temperatures at critical stages; pressure drop

especially over the filter. It may include also indicator means informing the engine operator, computer means effective to evaluate the data from the sensor(s), and control linkages effective to adjust the engine to desired operating conditions taking account of e g start-up, varying load and chance fluctuations.

Preferably the engine is a diesel engine, although other engines, including direct injection gasoline engines, may also benefit from the invention. The engine may be the motive power for a vehicle, or may be a stationary power source or auxiliary power source. It may be for a 'heavy duty' vehicle, ie at least 3500 Kg, or a 'light duty' vehicle, including in particular a passenger car or light van and likely to be operated according to the 'urban cycle'.

Desirably, the engine is fuelled with low-sulphur fuel, ie having less than 50ppm of sulphur, by weight as elemental S. For operation with higher sulphur fuels, a SO<sub>x</sub> absorbent may be used at some stage upstream of the NO<sub>x</sub> absorber.

The invention will be more fully understood from the following description of one preferred embodiment thereof, with reference to the accompanying drawing, which shows schematically in a single figure a system of catalysts and absorber suitable for carrying out the invention.

The system consists of single "can" 10, which is connected at 12 to the exhaust from a diesel engine (not shown) fuelled with diesel oil of under 50 ppm sulphur content. At the inlet end of can 10 is catalyst 14, which is a low temperature light-off oxidation catalyst supported on a 400 cells/in<sup>2</sup> ceramic honeycomb monolith. Catalyst 14 is designed to be capable of meeting emission regulations in relation to CO and HC for the engine and vehicle and also converts at least 70% of the NO to NO<sub>2</sub>.

The gas leaving catalyst 14 passes into soot filter 16, which is of the ceramic wall flow type and collects particles over 50nm. The NO<sub>2</sub> and surplus oxygen in the gas oxidise the soot at temperatures around 250°C with no accumulation or tendency to blocking.

The gas leaving filter 16 is passed over sparging spray injector 18, from which it

may receive regenerant fluid such as liquid reductant or NOx-specific reactant such as gaseous ammonia or ammonia precursor from supply tank 20 via line 22. Injector 18 is fed by pump 24 under the control of engine management system 26. Pump 24 suitably acts in a pulse mode and feeds NOx-specific reactant at a rate stoichiometrically equivalent to the NOx to be released.

The gas from 18, possibly carrying regenerant fluid, then enters NOx absorber 28. During normal lean operation of the engine and without injection at 18, absorber 28 substantially removes all NOx flowing. When, however, gas containing injected regenerant reaches it, the NOx is released, and is converted to N<sub>2</sub> to an extent depending on whether absorber 28 is catalysed. The gas, if still containing regenerant, NOx and O<sub>2</sub>, passes into 3-way catalyst 30, where these reactants are brought substantially to chemical equilibrium as non-polluting gases. If such reactions take place sufficiently over absorber 28, the gas leaving 28 is discharged to atmosphere. If a NOx-specific reagent is used as regenerant, catalyst 30 can be an SCR catalyst. Absorber 28 and catalyst 30 may be adjacent or mixed together on a single honeycomb.

The process and system of the invention is expected to be capable of meeting European Stage IV emission legislation, with all regulated emissions comfortably within the standards set.

### EXAMPLE 1

#### NOx-Trap Regeneration with Diesel Fuel

A NOx-trap comprising a 400 cpsi monolith having wall thickness of 6/1000 of an inch, measuring 5.66 x 6 inches, carrying a coating containing barium (13.2%), platinum (1.7%), rhodium (0.17%), with minor proportions of alumina, ceria and zirconia with a total loading of 3.5 g/in<sup>3</sup> was subjected to a CRT-treated gas stream from a 1.9 litre naturally aspirated direct injection diesel engine (Swedish MK-1 fuel) and containing NOx (260 ppm) at a catalyst inlet temperature of 310°C for 30 seconds during which time it began to become saturated with stored NOx. Upon introduction of MK-1 diesel fuel into the exhaust gas stream in front of the NOx-trap at a rate of 1 g/s for 3 seconds, the NOx-trap regenerated,



such that it was able to store NOx once more. The original operating conditions were restored whereby the same amount of NOx was stored, and this process was repeated many times without deterioration of the NOx capacity of the trap.

5

### **EXAMPLE 2**

#### **NOx-Trap Regeneration with EGR + Fuel Injection**

10 A NOx-trap as Example 1 was subjected to a CRT-treated gas stream containing NOx (145 ppm) at a catalyst inlet temperature of 220°C for 30 seconds during which time it stored NOx. The engine was as in Example 1, with EGR to reduce the oxygen concentration in the gas stream. MK-1 Diesel fuel was fed into the exhaust gas stream in front of the NOx-trap at a rate of 1 g/s for 1.5 seconds, to regenerate the NOx-trap: it was then able to store NOx once more. The original operating conditions were restored whereby the same  
15 amount of NOx was stored, and this process was repeated many times without deterioration of the NOx capacity of the trap.

Analogous successful runs were performed at other temperatures between 180°C and 330°C, with fuel injection for different times.

20

### **EXAMPLE 3**

#### **NOx-Trap Regeneration with Ammonia**

25 (a) A NOx-trap as Example 1, but also including palladium (1.7%) was subjected to a gas stream containing NOx (100 ppm), O<sub>2</sub> (9.55), CO<sub>2</sub> (8.2%) and H<sub>2</sub>O (9%) at catalyst inlet temperatures from 200° to 300°C for 60 seconds during which time it began to saturate with stored NOx. Upon introduction of ammonia (500 ppm) and cutting off O<sub>2</sub> for 60 seconds, the NOx-trap regenerated, such that it was able to store NOx once more. Original operating conditions were restored as Example 1.

30

In each of the above Examples the NOx trap outlet gas became rich during the regeneration period and was at a temperature at which a 3-way Pt/Rh catalyst would decompose NOx, HC and CO present in it.

(b) The run described in paragraph (a) was repeated but with the difference that for each temperature level the flow of gas was maintained with O<sub>2</sub> feed cut off and ammonia was injected only long enough to stabilise the temperature; this also fully regenerated the NO<sub>x</sub> absorber. Then the O<sub>2</sub> feed was resumed, initially for 60 seconds without ammonia injection (NO<sub>x</sub> absorption), then for 60 seconds with ammonia (regeneration); this alternation was maintained for 300 seconds.

Successive 300-second runs were carried out at stepped temperatures. The outlet NO<sub>x</sub> contents ppm v/v were:

150°-170°C:	30-40
200°:	30
250°:	25
300°:	25 rising to 45
350°:	25 rising to 100

it is evident that at over 300°C there is considerable side reaction of ammonia to NO<sub>x</sub>. However, at 150°-300°C absorption of NO<sub>x</sub> and regeneration by ammonia are effective, even in the presence of O<sub>2</sub>.

In each of the above Examples the NO<sub>x</sub> trap outlet gas became rich during the regeneration period and was at a temperature at which a 3-way Pt/Rh catalyst would decompose NO<sub>x</sub>, HC and CO present in it.

(c) By way of illustrating injection of ammonia upstream of the filter and use of the ammonia precursor urea, a part-system consisting of item 14 (oxidation catalyst) and item 16 (non-catalysed cordierite soot filter), was set up and equipped between 14 and 16 with a sparging spray injector fed from a reservoir of 32%w/w aqueous urea. The system included sensors for NO<sub>x</sub> and NO at engine outlet and 16 outlet. The inlet of 14 was fed with the exhaust of a 10 litre Volvo diesel engine. NO<sub>x</sub> levels were measured initially without urea injection, then at intervals during urea injection at approximate equivalence to the NO<sub>x</sub> in the gas as received, then after stopping urea injection. Runs were carried out at temperatures in the range 225°-350°C. Gas analyses for 290°C may be regarded as typical, and were as follows, measured in ppm v/v:

	NOx	NO	NO <sub>2</sub>
Engine-out	540	505	35
16 out (no urea)	525	200	325
5 16 out (urea)	400	160	240
16 out (urea stopped)	520	350	170
*****		check 170	350

10 It is evident that injection of urea has decreased the NOx content of the gas by only  
about 25%, leaving about 75% of the urea-derived ammonia available for use downstream of  
filter 16. In a system in which ammonia is to regenerate a NOx absorber, the ratio of  
ammonia to NOx at the inlet of 16 would be a 'spike', i e, much higher than stoichiometric  
and fully enough ammonia would reach the NOx absorber. Likewise, such a spike of  
15 ammonia, especially if added as urea, would sufficiently escape reaction over oxidation  
catalyst 14.

20

CLAIMS

1. A process for treating combustion exhaust gas containing CO, HC, NO, O<sub>2</sub>, soot  
5 and non-reactive gases, by the steps:  
i. catalysing oxidation of NO to NO<sub>2</sub>;  
ii. collecting soot on a filter from the product of i;  
iii. combusting the collected soot by reaction with NO<sub>2</sub> and possibly also O<sub>2</sub> left over after the  
reactions in i;  
10 iv. removing NO<sub>x</sub> from the product of iii by the action of a regenerable NO<sub>x</sub> absorbent;  
v. regenerating the absorbent intermittently by:  
(a) decreasing the net oxidant level by injecting reductant upstream of the absorber but  
downstream of the oxidation catalyst; and/or  
(b) injecting a NO<sub>x</sub>-specific reactant upstream of said absorbent; and  
15 vi. at least during said regeneration, subjecting the gas leaving the absorbent to a catalyst  
system effective to promote reactions of HC and CO with O<sub>2</sub> to H<sub>2</sub>O and CO<sub>2</sub> and to react  
NO<sub>x</sub> to N<sub>2</sub>.
2. Process according to claim 1 in which the NO<sub>x</sub> absorber comprises:  
20 (a) compounds of alkali metals, alkaline earth metals, rare earth metals and transition metals,  
capable of forming nitrates and/or nitrites of adequate stability in absorbing conditions and of  
evolving nitrogen oxides and/or nitrogen in regenerating conditions; and/or  
(b) adsorptive materials such as zeolites, carbons and high-area oxides.
- 25 3. Process according to claim 1 or claim 2 in which in the absorber the catalyst system of step  
vi is associated with the absorbent.
4. Process according to any one of the preceding claims in which the catalyst system in  
step vi includes a separate bed following the absorber.
- 30 5. Process according to any one of the preceding claims in which the catalyst  
associated with or following the absorber comprises vanadia/titania and/or one or more  
platinum group metals.

6. Process according to any one of the preceding claims in which reductant or reactant is introduced after step iii.

7. Process according to any one of the preceding claims in which the reductant is a hydrocarbon, hydrogen or dehydrogenatable organic compound.

8. Process according to claim 7 in which the air/fuel weight ratio of the exhaust gas containing injected reductant is in the range 10 to equivalence.

9. Process according to any one of claims 1 to 6 in which the NOx-specific reactant is ammonia or hydrazine and is injected as such and/or as a precursor compound decomposable thereto in situ.

10. Process according to claim 9 in which ammonia is injected as urea or aqueous urea solution.

11. Process according to claim 9 or claim 10 in which the reactant is injected into:  
(a) lean exhaust gas as generated by the engine or as issuing from a preceding step of exhaust treatment; or

(b) such gas to which reductant short of equivalence has been or is being added; or  
(c) gas made leaner, for example when the NOx-specific reactant is injected with the aid of air.

(d) rich or equivalent gas or gas into which reductant has been introduced eg to provide for reaction increasing gas temperature but leaving the gas net-lean in composition.

12. Process according to any one of claims 9 to 11 in which the reactant is injected upstream of the filter.

13. Process according to claim 12 in which the filter is non-catalysed.

14. Process according to claim 12 or claim 13 in which the reactant is injected upstream of the oxidation catalyst.

15. Process according to any one of the preceding claims in which the exhaust gas is the product of combustion of a fuel containing less than 50 ppm w/w of sulphur.

5 16. System for treatment of combustion exhaust gas having integers corresponding to the process according to any one of the preceding claims.

10 17. System according to claim 16 comprising, in combination and in order: a catalyst effective to promote oxidation of at least NO to NO<sub>2</sub>; a filter effective to collect soot and hold it for combustion reaction with the NO<sub>2</sub> in the gas; a NO<sub>x</sub> absorber charged with solid absorbent; means for introducing intermittently a regenerant of the absorber, such means being effective to introduce reductant upstream of the absorber but downstream of the oxidation catalyst; and/or to introduce a NO<sub>x</sub>-specific reactant upstream of the absorber; and, associated with and/or downstream of the absorber a catalyst system effective to promote reactions of HC and CO with O<sub>2</sub> to H<sub>2</sub>O and CO<sub>2</sub> and to react NO<sub>x</sub> to N<sub>2</sub>.

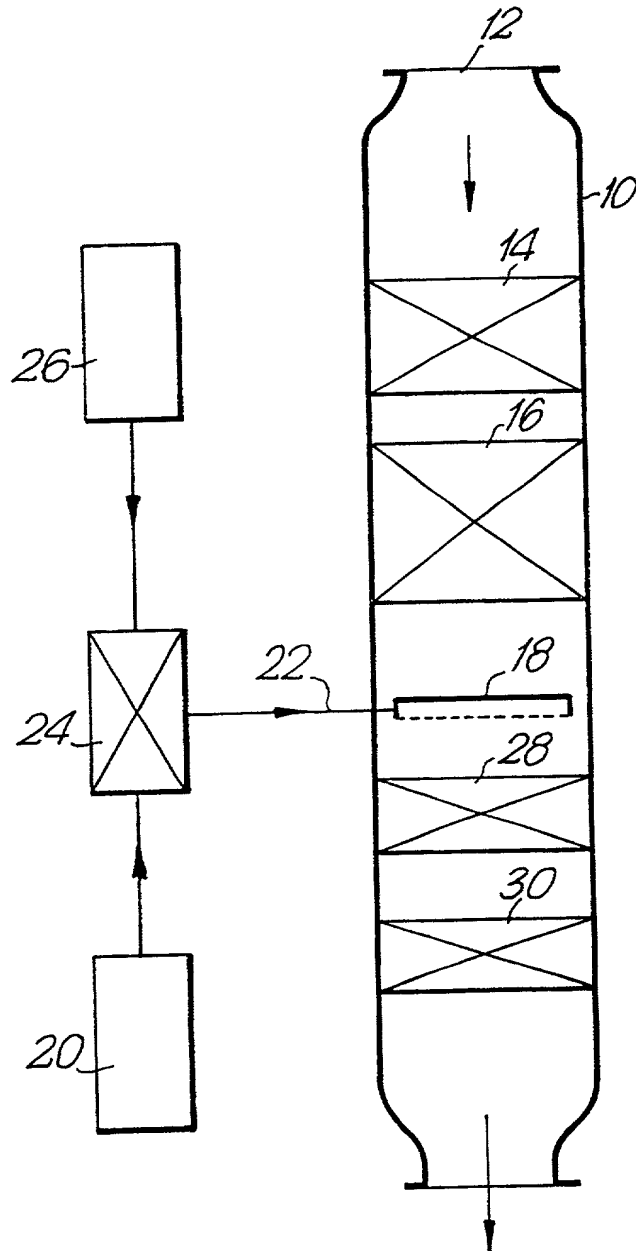
15 18. A diesel engine having a system according to claim 16 or claim 17 connected to its exhaust outlet.

20 19. An engine according to claim 18 which is of the turbo-charged direct injection type.

20. A process, system or engine according (as appropriate) to any one of the preceding claims, including sensors, indicators, computers and actuators, effective to maintain operation within desired conditions.

25 21. A process, system or engine substantially as described and as illustrated by the foregoing specific description.

30 22. A process, system or engine according (as appropriate) to any one of the preceding claims, operated in compliance with the European Stage IV emission legislation.



## Declaration and Power of Attorney For Patent Application English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled  
PROCESS AND APPARATUS FOR TREATING COMBUSTION EXHAUST GAS,  
the specification of which is attached hereto unless the following box is checked:



was filed on April 12, 2001 as

United States Application Number or PCT International Application Number 09/807,343  
and was amended on October 5, 2000, and by Preliminary Amendment on April 12, 2001  
(if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

9822083.3

Great Britain

October 12, 1998

(Number)

(Country)

(Day/Month/Year Filed)

☐

9917042.5

Great Britain

July 21, 1999

(Number)

(Country)

(Day/Month/Year Filed)

☐

Priority Not Claimed

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:



(Application Number) (Filing Date) (Status - patented, pending, abandoned)

(Application Number) (Filing Date) (Status - patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Additional inventors are being named on separately numbered sheets attached hereto.